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Polypyrrole

Formation and Use

Paul Saville

Defence R&D Canada – Atlantic

Technical Memorandum

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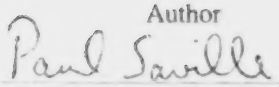

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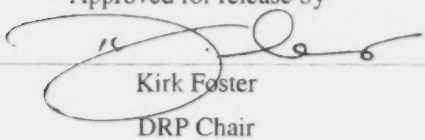

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Abstract

Radar absorbing materials require resistive or magnetic materials that will convert the electromagnetic energy into heat. The electrical properties of polypyrrole make it a suitable candidate for a radar absorbing material. There are several simple ways to make the polymer with controlled conductivity, and many strategies to process it into a robust material. Interesting materials include polypyrrole-paint, polypyrrole-polyvinylchloride injection moulded composites and polypyrrole coated fabrics and fibres. The highest imaginary component of the permittivity for a polypyrrole composite occurs at the percolation threshold. This is also the region where the permittivity changes rapidly with the amount polypyrrole in the composite and so a high degree of control is required for reproducible making the same formulation. At the conductivities required for microwave absorption, the dc conductivity dominates and the ac component is negligible. Polypyrrole stability is an issue for fabricating a radar absorber, and stability can be improved through a barrier protecting the polypyrrole from oxygen. In this paper many aspects of the formulation and characterisation of polypyrrole materials are considered with an emphasis on its suitability as a microwave absorber.

Résumé

Les matériaux absorbant les ondes radar doivent renfermer des substances magnétiques ou résistives, qui convertiront l'énergie électromagnétique en chaleur. Grâce à ses propriétés électriques, le polypyrrole est un bon candidat pour servir de matière absorbant les ondes radar. Il existe plusieurs manières pour synthétiser le polymère avec une conductivité déterminée et plusieurs stratégies pour le transformer en un matériau robuste. Parmi les matériaux présentant un tel intérêt, on retrouve des peintures au polypyrrole, des composites moulés par injection de type polypyrrole/poly(chlorure de vinyle) et des tissus et des fibres enduits de polypyrrole. La partie imaginaire la plus importante de la constante diélectrique d'un composite à base de polypyrrole est obtenue au seuil de percolation. C'est également la région où cette constante diélectrique varie rapidement en fonction de la quantité de polypyrrole dans le composite, et il est donc indispensable d'avoir un très bon contrôle du procédé pour obtenir une formulation reproductible. Aux conductivités requises pour l'absorption des micro-ondes, la conductivité c.c. prédomine, et la conductivité c.a. est négligeable. La stabilité du polypyrrole pose un problème lors de la fabrication d'un absorbant radar, et cette stabilité peut être améliorée au moyen d'une barrière protégeant le polypyrrole de l'oxygène. Dans le présent article, on rapporte divers aspects de la formulation et de la caractérisation des matériaux à base de polypyrrole, en mettant l'accent sur leur capacité à servir d'absorbant radar.

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Executive summary

Introduction

Radar is a highly sensitive detector. Its efficacy can be diminished, permitting operation at closer ranges and avoidance of threats, by reducing the reflected electromagnetic radiation. Conducting materials provide a mechanism for absorbing electromagnetic radiation. Polypyrrole is a conducting polymer that can be used.

Results

Polypyrrole is a conducting material whose properties can be tuned through chemical synthesis and composite processing. This paper reviews methods of synthesis, composite production, material characterisation and stability. The use of polypyrrole as an absorbing medium is reviewed.

Significance

Polypyrrole, if embedded in a coating that excludes oxygen, is a suitable for the formation of a radar absorbing material. Dallenbach layers can be formulated by incorporating the polymer into a coating or polymer composite, and wideband Jaumann absorbers can be made with polypyrrole coated fabrics.

Future plans

Polypyrrole materials will be made and evaluated for their functionality as microwave absorbers. Materials that will be studied include polypyrrole powders dispersed in a matrix, latex coated polypyrrole and fabric coated polypyrrole.

Saville, P. 2005. Polypyrrole : Formation and Use. DRDC Atlantic TM 2005-004.
Defence R&D Canada – Atlantic.

Sommaire

Introduction

Le radar est un détecteur très sensible. Il est possible de diminuer son efficacité en réduisant l'intensité du rayonnement électromagnétique réfléchi, permettant ainsi son opération à des portées plus courtes et l'évitement de menaces. Les matériaux conducteurs offrent un mécanisme d'absorption du rayonnement électromagnétique. Le polypyrrole est un des matériaux conducteurs qui peut être utilisé à cette fin.

Résultats

Le polypyrrole est une matière conductrice dont les propriétés peuvent être ajustées lors de sa synthèse et de son incorporation dans un matériau composite. Dans le présent article, on examine les méthodes de synthèse, la production de composites, ainsi que la caractérisation et la stabilité du matériau. On examine aussi l'utilisation du polypyrrole comme milieu absorbant.

Importance des résultats

Lorsque le polypyrrole est recouvert d'un revêtement étanche à l'oxygène, il peut servir à la production d'un matériau absorbant les ondes radar. Des couches de Dallenbach peuvent être formulées en incorporant le polymère dans un revêtement ou un composite polymère, et des absorbants à large bande Jaumann peuvent être produits avec des tissus recouverts de polypyrrole.

Travaux futurs

On synthétisera des matériaux à base de polypyrrole et on évaluera leurs caractéristiques en tant que matière absorbant les micro-ondes. Parmi les matériaux qui seront étudiés, on retrouvera des poudres de polypyrrole dispersées dans une matrice, du polypyrrole recouvert de latex et du polypyrrole recouvert de tissu.

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1. Synthesis of Polypyrrole

Polypyrrole is a conducting polymer that has attractive characteristics for the use as a radar absorbing material.[1] The polymer's conductivity can be varied over several orders of magnitude, covering a range that is suitable for microwave absorption.

In this paper, methods and the science behind the formation of polypyrrole are reviewed along with the published literature investigating the use of PPy as a radar absorbing material.

Polypyrrole (PPy) can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomer, Figure 1.

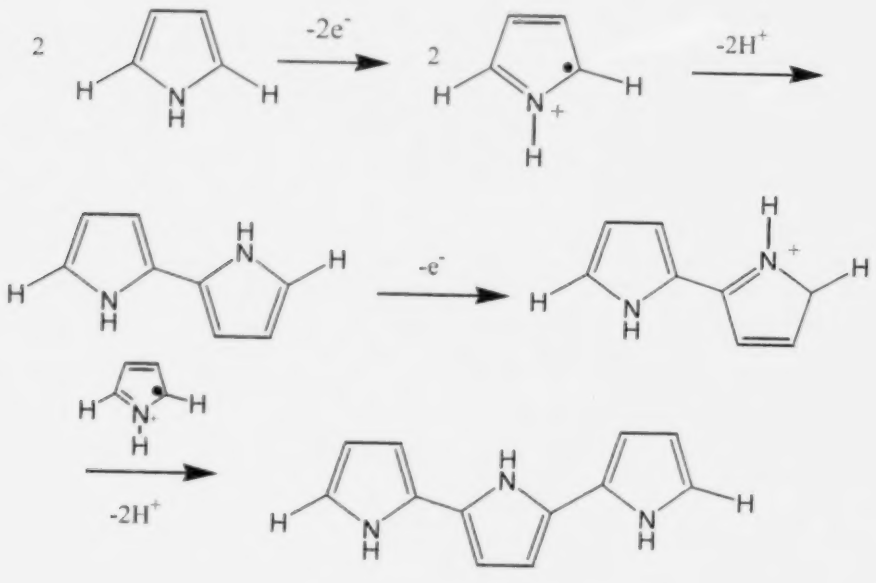

Figure 1. *Oxidative polymerisation of pyrrole to polypyrrole proceeds via a one electron oxidation of pyrrole to a radical cation, which subsequently couples with another radical cation to form the 2,2'-bipyrrole. This process is then repeated to form longer chains.*

The final form of polypyrrole is that of a long conjugated backbone as seen in Figure 2. The polymer has resonance structures that resemble the aromatic or quinoid forms. In this neutral state the polymer is not conducting and only becomes conducting when it is oxidized. The charge associated with the oxidized state is typically delocalised

over several pyrrole units and can form a radical cation (polaron) or a dication (bipolaron). The physical form of polypyrrole is usually an intractable powder resulting from chemical polymerization and an insoluble film resulting from electropolymerization.

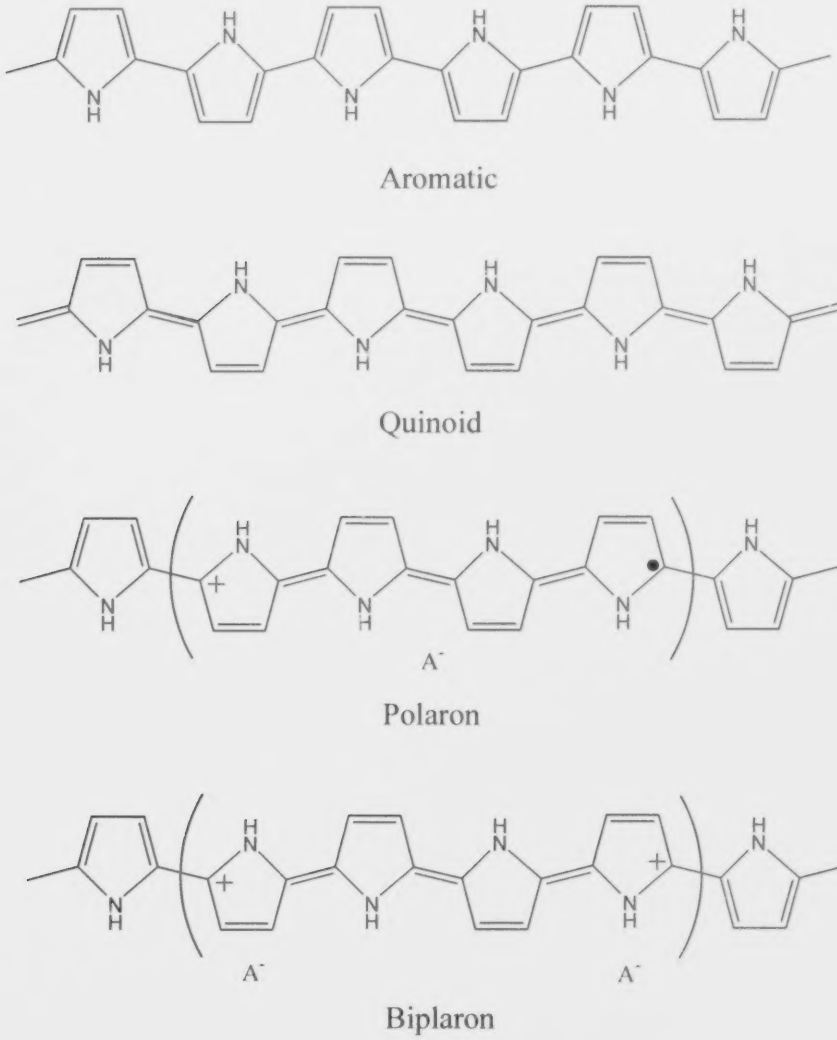

Figure 2. *Chemical structures of polypyrrole In neutral aromatic and quinoid forms and in oxidized polaron and bipolaron forms.*

1.1 Electropolymerisation of Pyrrole

Electrochemical oxidation of pyrrole forms a film of conducting polymer at the electrode surface. The electropolymerisation of pyrrole to polypyrrole precedes as follows, Figure 1:

Initiation. Formation of monomer radical cation by electrochemical oxidation, +0.8 V vs SCE.

Propagation. Combination of two radical cation monomers (or oligomers) followed by loss of two hydrogen ions. The linkage formed is at the 2 position of the pyrrole ring, forming 2,2'-bipyrrole. 2,5-disubstituted pyrroles do not polymerize and 2-monosubstituted pyrroles only form dimmers. Propagation continues by re-oxidation of the bipyrrole and further combination of radicals.

Termination. Occurs when no further monomer is present for oxidative polymerization or side reactions terminate the PPy chain. An example of a termination reaction is the reaction with water to form the amide group.

The success of electropolymerisation of pyrrole is due to the stability of the radical through charge delocalization, and the ease of electro-oxidation. The loss of the hydrogen ions makes the dimer (oligomer) formation irreversible so proton acceptors, such as water, pyridine and bases, enhance electropolymerisation. Good solvents for electropolymerisation[2] include water, acetonitrile, butanone, propylene carbonate, dimethylformamide (DMF) and ethanol though the presence of a bit of water (1 v/v%) enhances the polymer formation. Water can also result in chain termination.

Potentiostatic, potential cycling, and galvanostatic methods can be used to electropolymerise pyrrole. Potentiostatic methods (constant potential) and cycling the potential yield the most consistent films of about the same quality. Galvanostatic deposition (constant current), does not produce as good a quality film as the other methods, but is useful for controlling film thickness.

Electrochemical oxidation of a 5-member pyrrole oligomer[3] shows two reversible one-electron oxidation processes at E^o = -0.28 and -0.08 V vs Ag/Ag^+. These correspond to the formation of the radical cation and dication, respectively, which are stable and do not polymerize. Another oxidation peak at E_p=0.75 V marks the start of polymerization. Extrapolation of the E^o value to infinite chain length for the first one electron oxidation gives a value of –0.59 V, compared to the measured value of –0.57 V for polypyrrole from the pentamer.[3]

AFM studies of polypyrrole production indicate that time and substrate influence the final film morphology.[4,5] Supporting electrolyte was found to affect deposition kinetics.[5] Cyclic voltametry and NIR-Vis spectroscopy have also been used to show the affect of pH and counter ion.[6] Neutral polypyrrole is noted to be very unstable in water or air. In basic solutions the polymer was doped with hydroxide ions and other anions in acidic solutions. Incorporation of polymeric counter ions has been investigated for imbuing other properties such as thermoresponsiveness.[7]

1.2 Chemical Polymerisation of Pyrrole

Chemical synthesis of polypyrrole proceeds via the oxidation of pyrrole with an oxidant such as ferric chloride. The mechanism is similar to that for electropolymerisation of pyrrole and conductivities are comparable. The resulting polymer in its oxidized form is conducting with charge compensation afforded by $FeCl_4^-$. The conductivity of polypyrroles formed from different ferric salts (effect of dopant ion) has been related to the Fe^{2+}/Fe^{3+} redox potential with strong acid anions providing the most oxidizing ferric species. Weaker acid anions typically coordinate Fe^{3+} ions more strongly, reducing its oxidizing potential.[2] An investigation into the ferric ion equilibria in aqueous solutions showed that above a concentration of 0.5 M $HClO_4$ there was no change in the amount of available $Fe(H_2O)_6^{3+}$.[8]

The solvent the reaction occurs in also changes the redox potential. For example the Fe^{2+}/Fe^{3+} redox potential is lower in water than acetonitrile. If the redox potential is too high, an irreversible dissolution of polypyrrole can occur, as for ferric perchlorate in acetonitrile.[9] Methanol has been found to produce the best conducting polymer based on conductivity and morphology.[10,11] The conductivity was related to the redox potential of the Fe^{2+}/Fe^{3+} system and could be varied by adding $FeCl_2$. The optimum redox potential in methanol was +0.5 V vs SCE. The solvent also has an influence on the dopant ion that remains in the PPy film. In ether using $FeCl_3$ as oxidant leaves $FeCl_4^-$ as the dopant ion, while in methanol, the dopant is mainly Cl- with some $FeCl_4^-$.[2] Water was found to be trapped in the PPy with formation of pyrrolidinone rings at chain terminations similar to electrochemically produced films.[2]

Other counter ions to the ferric ion will also be incorporated into the PPy film[2] as will ions present in solution. Dopants whose bonds are labile such as Cl-O, B-F, P-F, should be avoided for sake of polymer stability.[12] Polymerisation of pyrrole in the presence of surfactants such as dodecylbenzyl sulphonic acid or a salt like sodium dodecyl sulphate, leads to an increase in mass yield due to incorporation of the salt/surfactant into the polymer.[13] Cationic surfactants were found to inhibit the polymerization of pyrrole. Polymerisation of pyrrole in the presence of polystyrene sulphonate (PSS) produced particles (non-colloidal) with the size being inversely proportional to the concentration of ferric chloride oxidant.[14] The size effect is due to the affinity of pyrrole and the ferric ion to PSS. The acid concentration affects the polymerisation process.

The conductivity of polypyrrole increases as the synthesis temperature is reduced. This is thought to be due to a reduction in the number of side reactions. Polypyrrole's conductivity as a function of temperature is studied as well as reflectivity, and classified into metallic, critical and insulating regions.[15]

The density of polypyrrole has been determined to be 1.48 g cm^{-3} and 1.44 +/- 0.05 g cm^{-3}.[14,16]

Polypyrrole derivatives have been prepared and their properties studied. By blocking the 3,4- positions on the pyrrole ring, unwanted side reactions at these sites are eliminated. This has been noted to yield higher conductivity in the case of poly 3,4-

dimethoxypyrrole.[17,18] Various alkylenedoxypyrroles have been synthesised and studied including a series of soluble species.[17,19,20] N-substituted pyrroles tend to induce twisting relative to adjacent pyrrole rings, thus limiting the conjugation length and conductivity. Solid state NMR has been used to elucidate some of the conducting mechanisms and structures.[21] Bipolarons appear to be the charge carriers and conductivity is linked to the loss or decomposition of the dopant ions. Elevated temperatures in air reduce the quinoid content and oxidise the 3,4-positions. Dodecyl sulphate is less stable than *p*-toluene sulphonate at elevated temperatures. Under argon the dodecyl sulphate doped film become brittle indicating cross linking at elevated temperatures.[21]

The polymer produced by electrochemical or chemical synthesis is generally an intractable solid or powder. The next section presents some of the strategies that have been investigated for the purpose of producing useable material.

2. Processability

Researchers have been looking at a number of methods for making conducting polymers practical. [22] The trade off is often lower conductivities, though sometimes there is the serendipitous gain of stability. Some of these methods include direct polymerisation onto polymers sheets, glass, polymer and inorganic particles, clays, zeolites, porous membranes, fibres and textiles and soluble matrices. The methods used to coat these materials are reviewed below to highlight potential avenues for the development of radar absorbing materials.

2.1 Solutions

The solubility of polypyrrole is limited due to its rigid structure and cross-linking. Attempts at increasing the solubility have been made by derivatizing the pyrrole ring at the 3- and 4- positions with alkyl groups, or substituents on the pyrrole's nitrogen. Another techniques that has been proven successful for some conducting polymers is to use long chain surfactant dopants like sodium dodecyl benzene sulfonate,[23-25] di(2-ethylhexyl) sulfosuccinate sodium salt,[26] or polystyrene sulfonate.[14] These polymers are then soluble in *m*-cresol, NMP, DMSO, DMF and THF.

2.2 Composites-Chemical Preparation

Since polypyrrole is generally intractable, attempts have been made to polymerize pyrrole onto or into the material where it is desired. In one strategy, the oxidant is mixed with the substrate and then exposed to pyrrole.[27] For instance, ferric chloride has been mixed with polyvinyl alcohol,[28], polyvinyl acetate,[29] polyethylene oxide,[30] poly(styrene-butyl acrylate-hydroxethyl acrylate),[31] poly(methyl acrylate-co-acrylic acid),[31] or rubber[32] and exposed to pyrrole vapours. The variation of this method is to soak the substrate with the pyrrole monomer and then immerse it in an oxidant solution.[27,33]

Polypyrrole can be deposited directly onto a substrate surface, by placing the object in a solution containing pyrrole and oxidant. This coating strategy has been applied to fabrics[34] and is discussed in greater detail below.

Surfaces have been derivatised with dopant groups to facilitate polypyrrole-substrate adhesion and deposition. Low density polyethylene has been sulphonated and used as a template for the polymerisation of pyrrole yielding PPy layers up to 80 nm thick and conductivity up to 150 S/cm.[35,36] A similar system was investigated using a sulphonic acid derivative of polystyrene grafted polyethylene,[37] and compression molded sulphonated polystyrene objects.[38] Other researchers have attempted to improve deposition and adhesion of the polypyrrole by graft polymerisation of other polymers to the polyethylene.[39] Polypyrrole has been deposited onto acrylic, polystyrene, polyimide and polyurethane foam.[22] Composites have been made by dispersing polypyrrole powder in melted LDPE, HDPE and PS,[40] or by dispersing polypyrrole

powder or flakes in silicone rubber or vinyl ester and curing the material.[41] Colloidal PPy has been made by stabilisation with methylcellulose.[42]

2.3 Copolymers and Graft Copolymers

Processable or soluble polypyrrole has been formed by graft copolymerisation of pyrrole. This has been accomplished by (i) coupling pyrrole to a reactive monomer, polymerizing the monomer and then polymerizing the pyrrole as was done for methyl-methacrylate,[43-45] or (ii) derivitization of a preformed polymer with pyrrole and then polymerizing the pyrrole as has been done for polystyrene-co-poly (chlorostyrene).[46] These materials were initially soluble with a tendency to become insoluble at high pyrrole content.

Direct copolymerization of pyrrole with other monomers has produced soluble conducting product. Examples include the polymerisation of pyrrole with various aniline derivatives,[47-49] and methyl ethyl ketone formaldehyde resin.[50] The conductivity and solubility depends on the feed ratio of pyrrole.

2.4 Composites-electrochemical

Pyrrole has been electrochemically copolymerised with a liquid crystal derivatised thiophene forming an insoluble film.[51]

2.5 Textiles

Conductive textiles[52] can be produced by weaving thin metallic or carbon wires, impregnating fibre materials with conducting powders, metallizing material, or by blending filament-sized fibres of stainless steel or carbon fibre. Conducting fibres have also been made from conducting polymers by solution spinning, however, they are typically brittle, expensive to produce and hard to manufacture on a large scale.[53] Conducting powder (carbon) incorporation is most cost effective, though the high content required to yield percolation reduces the mechanical properties of the fibres. Core/shell strategies, where normal textile fibres are coated with a conducting material, maintain the original mechanical strength. Conducting polymers have been use for this application, and yield conductivities that fall between metallized fabrics and carbon-based blends.

2.5.1 Conducting Polymer-Textile Formation

One of the earliest reports of the deposition of polypyrrole onto fibres involved a two-step process, whereby paper was soaked in a ferric chloride solution before immersion in a pyrrole solution.[33] Variations on this method include exposing the ferric chloride to pyrrole monomer in the vapour phase[54,55] and soaking the substrate in monomer

before polymerization in an oxidizing solution.[56] The process is also applicable to the use of various solvents.[57]

The easiest method of applying conductive polymer to a textile is from a solution of the conducting polymer. The solubility of highly conducting polymers (PPy, PANI and Polythiophene) is limited to solvents that are not generally compatible with the textiles.[25] Water-based systems have been used for coating textiles such as the PANI-PSS system and emulsion polymerized monomers to form latex.[58,59]

In-situ polymerization is another method for producing conductive coatings on textile substrates.[60-62] The mechanism for conducting polymer deposition proceeds through the adsorption of oligomeric species onto the textile surface, nucleation, from which subsequent polymerization occurs, growth, forming a smooth continuous film. Neither the monomer nor the oxidant is adsorbed to produce nucleation sites. In the presence of a fibrous surface, little or no polymer is found in solution. The coatings made by this method do not form significant fibre-to-fibre bonds, unlike solution and emulsion methods.

Polymer deposition is independent of surface material yielding films less than 1 um thick and very uniform for coverages of 1-5%. Substrate material does not have a significant effect on the polymerization of pyrrole, yielding essentially the same conductivity for the same mass of textile. Clean glass fabric is reported to not coat well with polypyrrole,[52] though its adhesion can be improved by the use of aminosilane or pyrrole-silane molecules that chemically bond to the glass surface.[63-65] Factors important to determining the conductivity include surface area, hydrophobicity, surface polarity and porosity. Porous fibres (nylon and polyacrylonitrile) and materials with polar groups tend to increase adhesion and polymer deposition while non-polar fibres such as polyethylene and poly tetrafluoroethylene and dense crystalline fibres such as polyester yield poorer adhesion. The conductivity is not a linear function of the mass of polypyrrole deposited.[52] Fabrics prepared from continuous filament yarns produce better conducting films than those prepared from spun fiber yarns.[66] The conductivity of PPy-Textiles does not vary greatly as a function of humidity.

Kinetics of the polypyrrole deposition on textiles has been studied.[61] The rate of polymerization is dependent on the concentration of monomer and type of oxidizing agent. Ammonium persulfate, APS, is much faster than $FeCl_3$. Acidic $FeCl_3$ is much faster than more basic $FeCl_3$ as the acid drives the equilibrium

$$Fe(H_2O)_6^{3+} \leftrightarrow Fe(H_2O)_5(OH)^{2+} + H^+$$

to the left. The hydrated species is smaller and not as tightly coordinated, so the reaction is more facile. Highly coordinating ligands or high pH slows the reaction rate. Comparing reactions with and without the presence of fibres in the reaction vessel, the reaction rate is faster with fibres present and second order, though first order reation rates can be achieved if the Fe^{3+} concentration is significantly increased. Without fabric, the reaction rate is second order and slower. Pure solvents such as methanol, methylene chloride or acetonitrile permit polymerization to occur in the solution phase, so no PPy is deposited on the fabric.

Pure solvents have already been noted to inhibit the deposition of PPy on the textile, whereas mixed solvents give mixed results. For instance, 20 g/L acetone in water inhibits PPy deposition, whereas the same concentration of methanol does not interfere. Textiles may be scoured with surfactants before sale and these may have an effect on PPy formation. Surfactants that are cationic or nonionic do not promote adsorption while dodecylbenze sulfonic acid, DBSA, marginally decreases adsorption. Hydrophobic surfactants such as alkylnaphthylsulfonate promote film formation. Other additives, such as 1,4-dihydroxybenzene, reduce adsorption while p-nitrophenol does not interfere. PPy – Fabric (Polyethyleneterphthalate and Polyethylene) samples have been chemically polymerized, using Poly (vinyl alcohol) as a surfactant to improve PPy coating on non-woven materials and NSA as a dopant with APS as oxidant.[15] The dc conductivity(T) indicates 3-d variable range hopping. Electrochemically treated PPy-fabrics in AQSA follow a power law where σ_{dc} is proportional to T^{β} indicating that the electrochemical treatment has induced charge delocalization.

Conducting fibres have been fabricated by electropolymerising pyrrole with a cotton, silk or wool fibre wrapped around the electrode.[67]

A considerable body of work exists for polyaniline, PANI, coated textiles.[68] Polyaniline on glass fibres has been studied.[60] The glass was cleaned in sulphuric acid to remove impurities before polymerization in HCl, aniline and PTSA. Conductivities up to 1.79 S/cm were realized based on the thickness of the film rather than the thickness of the fabric. It is pointed out here that in the rinsing stages of the PANI/HCl or PANI/PTSA fabrics, a solution containing the counterion must be used as rinsing with pure water leaches out the dopant.[69]

2.5.2 Microwave Properties of Conducting Polymer Coated Textiles

There are some literature reports of the microwave properties of conducting polymer composites.[70-74] Composites made from powdered carbon or metals do not have an appreciable effect on the lossy component to the complex permittivity, until the particles are nearly forming a percolative network. The tunnelling currents between adjacent particles render the material lossy. At the percolation threshold the particles are in contact and the material becomes conductive. The real part of the permittivity (the capacitance) increases as this type of composite is loaded with powder, whereas the imaginary component (loss) is small until the percolation threshold.

In contrast, for conducting polymer coated textiles, it is reported that the imaginary component of the permittivity can be varied over a large range without a great increase in the real component.[71] Looking at the data, the conductivity varies from 0-0.5 S/cm. A plot of σ vs ε' is nonlinear for PPy coated polyesters encapsulated in polyester resins over the frequency range of 26-40 GHz, whereas the same plot is

linear for PPy coated S-glass. Plots of ε'' vs ε' are linear with slopes of about 2.2 and 1.7 for PET and S-glass substrates respectively.

The use of paper and textiles coated with polypyrrole, have been studied for use as Salisbury screens and Jaumann layers.[72-75] High levels of polypyrrole loading on the textile or paper result in relatively frequency independent reflectivity, whereas light loadings are frequency dependent. These materials are modelled as a parallel RC circuit, where at high loading the sheets are mainly resistive and at light loadings sheet capacitance becomes the dominant term. Physically at light loadings, polypyrrole forms a uniform coating around the fibres of the textile and the capacitance is high. Heavy loadings result in the formation of particles on the textile surface, causing short circuits between fibre strands. These shorts reduce the capacitance and increase the conductivity. Formation of glass fibre and resin composites incorporating the PPy-textile sheets shows only small changes to the reflectivity.

2.6 Latex

Conducting polymer latex falls into two categories, pure latex and core-shell latex where a conducting polymer shell is coated onto an existing non-conducting latex core. Another area that falls into this general subject heading is that of conducting polymer nanocomposites which have been reviewed.[76]

Methylcellulose has been used to stabilise chemically formed polypyrrole, resulting in small particles dispersed in a methylcellulose matrix.[42] Similarly, PPy-Polystyrene sulfonate particles have been made by oxidizing pyrrole in presence of Fe^{3+}.[14] The size of particles is controlled by the Fe:Py ratio. Pure conducting polypyrrole lattices have been formed by the polymerization of the mononer in the presence of a steric stabilizer such as poly(vinylpyrrolidone), PVP, or poly (vinyl alcohol-co-acetate, PVA,[77,78] poly (2-vinyl pyridine-co-butyl methacrylate,[79] and a comprehensive study of a number of stabilizers.[80] Poly(ethylene oxide), PEO, polyacrylic acid and various block copolymers based on PEO, failed to provide steric stabilization. PANI latex has also been made and forms needle shaped particles.[68,81] Polypyrrole and polyaniline lattices and composite beads (PPy-PMMA) have been synthesized and cast into conducting films by mixing with a dispersion of a 1:1 copolymer of polymethylmethacrylaye-polybutylacrylate.[82] The PPy lattices were spherical and PANI lattices needle-like, giving percolation thresholds of about 20 and 5 wt% respectively. The surface energy of conducting polymers (PPy and PANI) is high, capable of strong interactions either via London dispersion or Lewis acid-base forces.[83] For PPy, the surface energy decreases within a few days, which is not seen for PANI. PMMA adsorbs to the PPy particles, forming a uniform coating when 1,4-dioxane is used as the solvent and a patchy coating when chloroform is used.

Conducting polymer-coated latex particles (core-shell) have been reviewed.[84] Conducting polymers based on pyrrole, aniline and EDOT, polymerized with ferric chloride, APS and ferric tosylate. Core lattices discussed are PS and PU[58,59]. Potential applications are found in anti-corrosion and anti-static coatings. High performance electrochromatography and novel marker particles for immunodiagnostic

assays.[85] PS/PANI core/shell lattices have been made in the presence of Polyvinylpyrrolidinone,[83,86] and SDS (sodium dodecyl sulfate).[47] PPy deposits onto submicron poly (ethylene glycol) stabilized PS latex as nanoparticles, bridging the PS particles and causing flocculation.[87] Other PANI/PS-co-PSS lattices have been made.[88]

Nanocomposites of conducting polymers (PPy and PANI) and iron oxide magnetic particles have properties different from pure magnetic particles.[89] Electrophoretic mobilities of glass beads coated with PPy in the presence of a nonionic surfactant Rhodasurf TB970, have been measured.[90] 20 nm Silica colloidal particles have been coated with PPy,[86] and PANI[91,92]. Both of these produced agglomerates of silca and conducting polymer giving a raspberry like structure. Carboxylic acid derivatized polypyrrole-silica composites showed improved colloidal stability.[93]

A reverse core-shell PPy/polyacrolein latex has been synthesized and studied by atomic force microscopy, AFM.[94] The surface of the PPy particle was not completely covered by the polyacrolein.

2.7 Improved Adhesion to Inorganic Substrates

The adhesion of polypyrrole to the substrate has been discussed above in reference to using anionic surface groups to act as templating and dopant sites. When it comes to the fabrication of structural materials, it is important that all the layers in the composite are well bonded in order to avoid delamination. For this reason the promotion of adhesion to glass fibres and other inorganic materials has been investigated. [63,65,95] These papers present pyrrole-siloxane molecules for the promotion of adhesion to glass surfaces through coupling of the siloxane to hydroxyl groups on the glass. The pyrrole monomers are then polymerised with extra pyrrole from solution to form a conducting layer. Layer thickness vs conductivity results[95] indicate increasing conductivity to a particular thickness, while other results indicate the siloxane coupling agent promotes higher conductivities than other adhesion promoting agents. [63] Pullout failure of pyrrole coated glass fibres, with siloxane adhesion promoters, embedded in a polymer matrix showed similar failure loads to uncoated glass fibres and no failure at the glass-polypyrrole interface.[63] This surface treatment has also been used for coating silica gel for chromatography purposes.[96]

2.8 Tubules/Fibres

Polypyrrole tubules have been synthesized chemically and electrochemically by growth within a pore or by using surfactant mediation. Pore templated growth of PPy tubes has been accomplished by polymerisation within the pores of porous alumina[97] and polycarbonate[98-101] membranes. Selective dissolution of the membrane results in PPy tubules. A two-probe method for measuring the tubule resistance (conductivity) is given with conductivity decreasing for thicker tubes. The centres of the tubules tend to be filled with less well-ordered polymer.

A number of surfactant systems have been used to template the growth of polypyrrole tubules. A reverse microemulsion system using sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was found to form nanotubes about 95 nm wide and up to 5 μm long.[102] Naphthalene-2-sulphonic acid also acts as template for polypyrrole growth (chemical or electrochemical) with a range of morphologies dependent on the surfactant concentration.[103,104] Diacetylenic phospholipid tubules template polypyrrole growth, however, it tends to be at the seems or edges of the lipid tubules, rather than coating the walls.[105] Polymer fibrils have also been detected in electrochemical deposits with *p*-Toluene sulfonic acid as the dopant.[106]

3. Material Characterisation

3.1 Spectroscopy of Polypyrrole

UV/Vis spectroscopy of oxidized polypyrrole (conducting) shows two absorbance maxima at about 430 and 900 nm. These two peaks have been attributed to transitions of the valence to polaron and bipolaron/polaron states. Extrapolation of λ_{max} for the first one-electron oxidation peak of oligomers, to infinite chain length, gives the optical transition E_g of 2.81 eV or 435 nm and polymerised product yielded 435 nm [3] The ratio of the two absorbance maxima mirrors the doping level of the polymer which in itself is dependent on the degree of oxidation and the length of conjugation. An electrochemically grown tosylate doped polypyrrole film was reported to have a ratio of 1.6.[107] This ratio decreases if the polymer is reduced or over oxidized. Reduced polypyrrole has an absorption band at about 410 nm which is assigned as the $\pi \rightarrow \pi^*$ interband or valence to conduction band transition.

More recent UV/Vis measurements of electrochemically grown polypyrrole[108] and theory indicate four possible states for polypyrrole existing all at the same time. These states are the neutral polymer, polaron (radical cation), bipolaron (dication) and transverse bipolaron. This latter class describes polarons on adjacent chains that couple to form "transverse bipolarons". The bands at 1.4 and 1.8 eV are assigned to the sum of the polarons and transverse polarons. The band at 2.44-2.5 eV is assigned to the sum of the polarons, bipolarons and transverse bipolarons, and the band at 3.2 to 3.6 eV is due to the bandap of polypyrrole.

3.1.1 IR-Raman spectroscopy of polypyrrole

If PPy is considered as a chain of coplanar pyrrole units in the anti conformation, then the one dimensional lattice is of the D_{2h} point group with 16x3-4 normal modes.[109] These are as follows

In-plane modes: 8 Ag (Raman polarised) + 8 B1g(Raman dep) + 7B2u(IR) +7B3u(IR)

Out-of-plane modes: 3 Au(inactive)+4B1u(IR)+3B2g(Raman dep)+4B3g(Raman-dep).

There is a vibration, termed the R vibration, which corresponds to the expansion / shrinking of the bonds representing the HOMO "aromatic" structure and LUMO "quinoid" structure of PPy, and this leads to modes that are apparent in the Raman. Of the Raman modes, only those that are symmetric tend to produce a noticeable absorption. For PPy calculations have predicted that only three of the totally symmetric modes will be Raman active.[109]

The effective conjugation lengths of pyrrole oligomers and pyrrole were measured.[3,109-113] The main bands are listed in Table 1. What is interesting is the

presence of bands, which can be assigned to the oligomer chain-ends and these are still apparent for polypyrrole.[109] The work with oligomers shows an increasing delocalisation of the π-electrons with increasing conjugation length. This indicates a 0° conformational angle between the inter-ring carbon bonds. The effective delocalisation length appears to reach a limit at 7-9 pyrrole rings. Protecting groups on the pyrrole cause a distortion to the planarity of the rings (inter-ring angle of 70°) though there is indication of delocalisation.[3]

Table 1. IR and Raman absorption frequencies.

IR FREQUENCY OF ABSORPTION cm^{-1}	RAMAN FREQUENCY OF ABSORPTION cm^{-1}	ASSIGNMENT
3558		O-H stretching covalently bound due to lack of O-H bending at 1620 cm^{-1} in undoped PPy [112]
3400		N-H stretching
3110		Aromatic C-H stretching
	1557 (S)	Ag R vibration
1547		C=C stretching
1497		
1440		C-C, C-N stretching
	1312	Ag
1310		Mixed bending and stretching vibrations associated with C_N links
1223		
1180		C=N stretching
1115		C-O vibration for undoped PPy[112]
	1037	Ag
1035 (1043)		N-H wagging
759		N-H wagging

3.2 Characterisation of Polypyrrole's Permittivity and Conductivity at Microwave Frequencies

The permittivity of a material is a function of frequency, and it depends on the conduction and polarisation processes within the material. In the case of conducting polymers the observed loss characteristics are due to conduction processes,[1] which depend on inter- and intra-chain charge transport. Decreasing polymer defects and increasing chain length increase intra-chain transport, while decreasing dopant and polymer substituent size and increasing pressure increases inter-chain transport. These effects have a direct bearing on the real and imaginary components of the permittivity. ε' and ε'' both increase with increasing polymer chain length and decreasing defect number. Increasing the chain separation by dopant, substituent or lower pressure, lowers the values of ε' and ε''.[1]

Permittivity results have been presented for polypyrrole powder and electrochemically prepared polypyrrole flakes dispersed in silicone rubber and vinyl ester as a function of volume percent polypyrrole.[41] The composites were found to be conductive if the powder aggregated in the silicone rubber before setting. The pyrrole flakes do not form a percolating network even at high loadings. Increased conductivity of the polypyrrole used in the composite resulted in higher values of ε'. This higher permittivity was assigned to the increase in interfacial polarisation between dispered particles and insulating matrix.[41] When the conducting medium is isolated from other particles the conductivity of that material has little overall effect on ε'', compared to composites where a percolation path is established. Surface tension of the conducting and insulating matrix phases will facilitate aggregation if there is a large mismatch, and will facilitate dispersion if they are similar. Silicone rubber has a very low surface tension. Particle size will also favour aggregation if the particles are small, due to the interfacial energy gained upon dispersing small particles.

4. Conducting Nature of Polypyrrole

Charge carriers in polypyrrole result when the neutral, non-conducting polymer is oxidized, leading to a polaron or bipolaron states. [114]

A conducting polymer is generally thought of as a disordered material, though exceptions exist.[115,116] In the undoped state there are no conduction paths ($\sigma_{dc} = 0$). As the polymer becomes partially doped, islands of conducting material develop which are oxidized sites on the polymer chains. These sites are generally fixed by structural disorder and dopant and generally isolated from each other. A small percentage of the sites will form a network across the material, yielding a small, finite dc (static) conductivity. Tunneling or hopping of charge carriers between sites (islands) in the polymer (variable range hopping model, VRH) accounts for the ac conductivity or intra/interchain conduction noted at higher frequencies. The total conductivity is thus a combination of the frequency dependent and dc conductivities. Higher doping levels increase the network density through the polymer and at the same time eliminating the number of isolated sites that give rise to the ac conductivity. At the limit of very high doping levels the number of isolated sites is at a minimum and the dc conductivity dominates the total conductivity.

For conducting polymers the conductivity is both temperature and frequency dependent.

4.1 Temperature Dependence of Conductivity

The temperature dependence of the dc conductivity[115,116] of conducting polymers tends to follow the Variable Range Hopping model's prediction of

$$\sigma = \sigma_o \exp\left[-\left(\frac{T_o}{T}\right)^{1/4}\right] \qquad 1$$

where

$$\sigma_o = e^2 R^2 \nu_{ph} N(E_F)$$

$$T_o = \frac{\lambda \alpha^3}{kN(E_F)} \qquad 2$$

and T_o is the characteristic temperature, e is the electronic charge (1.602×10^{-19} C), k is Boltzmann's constant (8.616×10^{-5} eV/K), R is the average hopping distance (cm) ν_{ph} is the phonon frequency ($\sim 10^{13}$ Hz), $N(E_F)$ is the density of localized states at the fermi level ($cm^{-3}\ eV^{-1}$), λ is the dimensional constant (~18.1) and α is the coefficient of exponential decay of the localized states (cm^{-1}).

A plot of ln (σ) vs (T)$^{-1/4}$ is a straight line for a number of conducting polymers. For lightly doped polypyrrole, the average hopping distance, R, was calculated to decrease from 1.6 to 0.44 nm at 300 K and 3.7 to 1.0 nm at 10 K for increasing dopant levels. These numbers equate to 5 - 1.5 and 12 - 3 monomer units at each temperature.[117]

4.2 Frequency Dependence

Low frequency methods (10^{-2} – 10^{7} Hz) of measuring electrical relaxations in a material yield the equivalent parallel conductance, G, and capacitance, C. These terms then define the complex permittivity, ε*, conductivity, σ*, resistivity, ρ*, and complex modulus, M*.

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{1}{M^*} = \frac{\sigma^*}{i\omega\varepsilon_o} = C - \frac{iG}{\omega\varepsilon_o} \qquad 3$$

$$\sigma^* = \frac{1}{\rho^*} = G + i\omega\varepsilon_o C \qquad 4$$

$$\rho^* = \rho' - i\rho'' = \frac{G}{G^2 + \omega^2\varepsilon_o^2 C^2} - i\frac{\omega\varepsilon_o C}{G^2 + \omega^2\varepsilon_o^2 C^2} \qquad 5$$

$$M^* = \frac{\omega^2\varepsilon_o^2 C}{G^2 + \omega^2\varepsilon_o^2 C^2} + i\frac{\omega\varepsilon_o G}{G^2 + \omega^2\varepsilon_o^2 C^2} \qquad 6$$

From studies of dielectric relaxation on mobile charge carriers, a contribution to the permittivity is assumed to arise from the mobile charge carriers that is frequency dependent

$$\varepsilon''_\sigma = \frac{\sigma_{DC}}{\omega\varepsilon_o} \qquad 7$$

where σ_{DC} is the static or low frequency conductivity of the material and accounts for long-range charge transport. This expression is often subtracted from the imaginary component of the permittivity to account for dielectric relaxation processes not involved in long-range charge transport. The resultant expression for the complex permittivity is

$$\varepsilon^* = \varepsilon' - i\left(\varepsilon'' - \frac{\sigma_{DC}}{\omega\varepsilon_o}\right) \qquad 8$$

This equation makes the assumption that the transport mechanism, leading to long-range DC conductivity, has no influence on the complex permittivity other than the

contribution from equation 6. This in turn implies that the conductance process can be defined by one relaxation time, τ_σ,

$$\tau_\sigma = \frac{\varepsilon_o \varepsilon_s}{\sigma_{DC}} \qquad 9$$

For a disordered system such as a conducting polymer, or conducting composite, a distribution of relaxation times, $\langle \tau \rangle$, is more appropriate.

$$\sigma_{DC} = \frac{\varepsilon_o \varepsilon_s}{\langle \tau \rangle} = \frac{\varepsilon_o}{M_s \langle \tau \rangle} \qquad 10$$

where M_s is the static modulus or the reciprocal of the static permittivity.

From the above discussion of the conduction mechanisms it is clear that the conductivity of polypyrrole is also dependent on the level of doping (oxidation) and the frequency. The total conductivity of a material is the sum of the ac and dc components

$$\sigma_{Total} = \sigma_{ac} + \sigma_{dc} \qquad 11$$

For lightly doped polypyrrole films, the ac conductivity is larger than the dc when the frequency is high due to conduction by hopping transitions. At low frequencies the dc conductivity is larger and dominates charge transport due to the charge carriers having time to cross the sample following the percolation network. At high dopant levels the dc conductivity dominates and the total conductivity is frequency independent.[117] The imaginary component of the permittivity is related to the ac and dc conductivity by the equation

$$\varepsilon'' = \frac{\sigma_{ac} + \sigma_{dc}}{\omega \varepsilon_o} \qquad 12$$

4.3 Conductivity of Composites

For a polypyrrole poly(methyl methacrylate) composite above the percolation threshold, the conductivity shows different behaviour in three frequency regions. At low frequency, the conductivity is frequency independent and follows the scaling law

$$\sigma = A(p - p_c)^t \qquad 13$$

where p and p_c are the weight fractions PPy in the composite and at the percolation threshold, respectively, t is the percolation exponent (t has a theoretical value of 2 for percolation) and A is a constant related to the bulk conductivity of the PPy, (ie at $p = 1$, $\sigma = \sigma_{PPy}$). Experiment gave an exponent t of 1.95.[118]

At intermediate frequencies, MHz-GHz, a relaxation transition has been observed and attributed to space-charge relaxation. Above the percolation threshold an infinite cluster exists as well as finite and isolated clusters of all sizes. The mean size of finite clusters, L, is governed by percolation theory and varies as

$$L \propto (p - p_c)^{-\nu} \quad \text{at } p < p_c. \qquad 14$$

Charge transport in this region is diffusive and the imaginary permittivity peaks at a frequency of

$$f_{max} = \frac{D}{2\pi L^2} \qquad 15$$

where D is the diffusion coefficient of the charge carrier. From this equation it is seen that the maximum frequency is dependent on the length of the clusters, L. This is why ε'' peaks at the percolation threshold, where L is at a maximum. It can be shown that

$$f_{max} \propto (p - p_c)^{2\nu} \qquad 16$$

where the theoretical value of ν is 1 for percolation theory and experiment give $\nu = 1.2$.[118]

At high frequencies, >1 GHz, the ac contribution to the conductivity results from the hopping process and is given by

$$\sigma_{ac} \propto \omega^{x} \quad \text{where } x > 0 \qquad 17$$

$$\varepsilon'_{ac} \propto \omega^{y} \quad \text{where } y < 0 \text{ and x-y = 1.} \qquad 18$$

Composites of PPy-PMMA follow this behaviour.[118]

Pelster and Simon study and review dispersions of nano conducting particles in a matrix.[119] The conductivity is related to the penetration depth, δ, of electromagnetic radiation into a material by the equation

$$\delta = \sqrt{\frac{2}{\omega\sigma\mu}} \qquad 19$$

where ω is the angular frequency, 2πf, and μ is the permeability of free space.[120]

5. Polypyrrole Stability

The conductivity of polypyrrole is not as stable, with respect to time and temperature, as one would like. A variety of analytical and spectroscopic techniques have been used to try to elucidate mechanisms that result in decreased conductivity and attempts have been made to improve the polymer's useful life.

UV/Visible spectroscopy has been used to study the charge carrier species of freshly electro-polymerised polypyrrole. Over the first 90 minutes while the film was still drying, an increase in the sum of polarons, transverse bipolarons and bipolarons was observed. The spectra also showed a decrease in the amount of polarons or transverse bipolarons though the overall change is small, at most 6%.[108] These samples were then heated above the glass transition temperature, T_g, for PPy at 80° C for 35 hours, allowing the polypyrrole to form more structurally favourable confirmations. In this case more polarons and neutral polypyrrole is observed along with a decrease in the amount of the transverse bipolarons. Polypyrrole doped with dodecyl sulphate initially behaved differently on heating than polymer doped with *p*-toluene sulponate. The polymer and material were observed to undergo a phase change, increasing crystallinity, before the high temperature resulted in a collapse of the structure.[108] Cooling the samples showed a reversal of the changes in carrier population effected upon heating. This study does not consider the degradation of the polypyrrole, or it's conductivity, however, it does elucidate changes in charge carriers that might be more susceptible to oxidation. The rest of the review on thermal degradation will consider specific systems.

The temperature and dopant ion have large roles to play in the stability of polypyrrole. Solid state NMR[21] of polypyrrole films at 150 °C indicates the loss of dopant ion accompanies the loss of conductivity. Dodecyl sulphate, [21,121] decomposes on heating, possibly leaving a sulphate ion and tends to cross-link the polypyrrole in an inert atmosphere. This dopant ion was observed to be less stable than *p*-toluene sulphonic acid. Infrared and mass-spectral data taken during the thermal degradation of electrochemically grown polypyrrole doped with *p*-toluene sulphonic acid, indicate a high concentration of oxygen defects. In the initial stages H_2O, CO, CO_2 and $CH_3C_6H_4$ are evolved, though SO_3^- could not be resolved and no evidence of pyrrole was seen.[122] At higher temperatures evolution of HCN and SO_2 was evident.[121,122]

DSC measurements have been made of *p*-toluene sulphonate and dodecyl sulphate doped polypyrroles.[123] The *p*-toluene sulphonate doped polymer appears to undergo a water-plasticized endotherm at that is dependent on the method of film preparation. Above 100° C there is evidence of water loss. For dodecyl sulphate films a similar endotherm may be due to a surfactant induced phase change as noted by crystallography.[108]

Mechanical and electrical properties of aged polypyrrole have been made.[124] Aged samples quickly became stiff and brittle probably due to egress of plasticizing solvent from the film. Highly doped polypyrrole had a lower breaking stress than lightly

doped material due to the crack propagating along granular boundaries found in the highly doped film. Lightly doped films were noted to be smooth.[124]

At room temperature chemically formed polypyrrole is less stable than that formed by electrochemical methods due to a larger surface area.[40] When the polypyrrole powder is dispersed in polymer matrices, such as LDPE, HDPE or polystyrene, the conductivity behaviour depends on the glass transition temperature of the polymer. For LDPE and HDPE, annealed at 55 or 80° C (higher than T_g), the conductivity steeply decreased before reaching a steady state. It is surmised that the thermo-expansion and mobility of the matrix allows it to encapsulate the conducting particles. Polypyrrole dispersed in polystyrene and annealed at these temperatures had a very stable conductivity.

Conducting polymers have a high reactivity to oxygen, which disrupts the percolative networks and reduces conductivity.[125] Exclusion of oxygen with nitrogen, or by encapsulating the polymer in a protective coating, decreases conductivity loss. Examples of potentially useful oxygen barriers include poly (vinyl chloride), paraffin, poly (vinylidene chloride)-poly(acrylic acid) copolymer, poly (vinylidene chloride, polyester and polyolefin.[126,127] Epoxy resin has also been used to encapsulate PPy coated textiles.[128] In the absence of oxygen, the rate of conductivity decrease is greatly reduced and seems to be dependent on Cl^- ion content in the films. PPy prepared from $Fe(PTSA)_3$ does not lose conductivity at elevated temperatures, whereas codoped Cl^- and PTSA films do, though at a lower rate than in the presence of oxygen.

Kinetics of PPy-textile degradation has been studied as a function of dopant ion (Cl^-, PTSA, NDSA, N2SA, AQSA).[129] The degradation process was found to be diffusion controlled and first order. For polypyrrole this is thought to be due to the polymer having a high concentration of polarons (free radical sites) [108] and since oxygen adsorption is assumed faster than reaction with the polymer backbone, so first order kinetics are observed. Other studies have shown an increase in carbonyl functionality during degradation though with no accompanying mass increase. This would follow the suggestion that hydroxyl groups are incorporated in the structure during chemical polymerization.[112] Subsequent stability studies have indicated that the conductivity degradation is controlled by the diffusion of the oxidizing species into the film.[121,130-132] Diffusion control is applicable at short times with the reaction rate becoming first order at long times.[129]

Polypyrrole morphology and stability is dependent on its composition.[133] Conducting films made with ferric chloride have chloride counterions (dopant), which has a higher mobility than other counterions. Chloride ion doped films tend to dedope at elevated temperatures in contrast to other less mobile ions. Adding other suitable salts (eg sodium salts of aryl sulfonates) results in films containing mixed dopants. Elimination of chloride ions from the film can be achieved by using other ferric salts of the arylsulfonates.[2] These hydrophobic dopants tend to form more compact, stable and conducting films which is due in part to their planar structure, though it is surmised that the hydrophobic nature may favour their thermodynamic incorporation in the film.[129] In the case of anthraquinone-2-sulfonic acid salts, AQSA, it may be more a question of working near the solubility limit of the AQSA in water that favours its

incorporation in the film.[66] Studies of the atomic ratios of Cl/N for films made with $FeCl_3$, PTSA and AQSA show a decreasing trend in the amount of chlorine in the films, while the S/N ratio shows an increasing trend in the sulfur content. The total (S+Cl)/N increases to 0.34 for AQSA which is effectively the doping limit of one counterion per three monomer units. Another ratio that has been looked at is the O/N ratio which is smallest for the AQSA films. Some of the oxygen will come from included water[2], and some from chain termination reactions forming pyrrolidinone. Another possible source has been identified as nucleophilic hydroxyl substitution of the pyrrole rings.[112]

Scanning thermogravimetric analysis measurements made of PPy coated PET show mass loss at 400° C, which is the same as pure PET. Isothermal TGA at 300 C show greater mass decreases for PPy Coated PET than pure PET.[134]

6. Polypyrrole use in Radar Absorbing Materials

A big issue with the preparation of radar absorbing materials from polypyrrole is the process by which the material is made. Polypyrrole dispersed in a matrix yields very different permittivity characteristics than does in situ composite formation.[1]

6.1 Dallenbach Layers / Polypyrrole Composites

One of the few references that presents permittivity, conductivity and reflectivity data for polypyrrole, shows that processing has a great effect on the final product.[135] Polypyrrole/PVC composite was compressed and melt injected into sheets. The compressed material was macroscopically conductive with $\varepsilon^* \propto K\omega^{-s} = \frac{\sigma(\omega)}{\omega\varepsilon_o}$, where K is a constant and the conductivity is frequency dependent. The melt-injected material was macroscopically insulating with Maxwell-Wagner type relaxation. The relaxation frequency is given by $f_r = \frac{\sigma_2}{2\pi\varepsilon_o(2\varepsilon_1' + \varepsilon_2')}$, where the subscript 1 denotes the properties of the matrix and 2 the conducting phase. The compressed material is difficult to make into a tuned absorber , while the melt injected material readily forms a resonant Dallenbach layer.[135] This material shows a very narrow absorption with more than –40 dB reflectivity.

Dallenbach layers have also been made from polypyrrole doped with *p*-toluene sulphonic acid sodium salt, or 5-sulfosalicyclic acid dehydrate.[136,137] The chemically prepared powder was dispersed in a commercial paint, or milled with natural rubber and moulded into flat sheets and both were applied to an aluminum backing panel. These materials show resonance absorption if the content of the conductive powder is not below the percolation threshold. The rubber composites, and inclusion of conducting fibres that did not produce a macroscopically conductive material, still had a reasonable high value of ε'' and were therefore useful in making Dallenbach layers. A hybrid dielectric/magnetic material was also made using carbonyl iron, however, extra bandwidth was not realised for this material. [136,137] Powder processing was noted to have an influence on the final material properties.

Materials with conductive gradients have been made. [137] Phenolic foam, with a pore size on the order of 1 μm, was soaked in aqueous ferric chloride and then exposured to pyrrole vapour from one side. The gradient was obtained by controlling the exposure time. Uniformly coated foam was prepared by immersing the oxidant doped foam in an aqueous pyrrole solution and flowing the pyrrole solution through the foam. The permittivity of the foam was measured and showed very low values of ε_r' in the range of 1-2 and good values of ε_r'' in the range of 0.5-10. Two problems are associated with vapour polymerization, a thick coating on one surface of the foam and poorly

conducting polymer doped with chloride from the ferric chloride. The wet method produced a material with better properties and a gradient could be induced into the material. It was noted that a 15 mm thick foam prepared in this manner [137] performed better than other published gradient absorbers.[138,139]

Paper, cotton and polyester fabrics have been coated with polypyrrole as discussed above. [72-75] Modelling the reflectivity from the material alone, with a Resistance-Capacitance model, shows some interesting properties.[140] The capacitance of the material increases with increasing loading of polypyrrole on the fabric, until granular deposits form which are thought to short circuit the fibres. The conductivity still increases with increased loading, however, the capacitance was observed to decrease.[72,75,141] These materials have been made into Salisbury screens and Jaumann layers. The presence of capacitance in the material allows for additional design control with the production of thinner absorbers. Asymmetric weave has a polarisation effect.[140] The effect of incident angle and polarization were measured and presented.[74]

Polypyrrole coated textile fibres have been considered as replacements for metallised fibreglass chaff. With the correct chemical composition the impact on the environmental and accelerated degradation could be limited.[133]

7. Conclusions

The electrical properties of polypyrrole make it a suitable candidate for a radar absorbing material. There are several simple ways to make the polymer with controlled conductivity, and many strategies to process it into a robust material. Interesting materials include polypyrrole-paint, polypyrrole-polyvinylchloride injection moulded composites and polypyrrole coated fabrics and fibres. The highest imaginary component of the permittivity for a polypyrrole composite occurs at the percolation threshold. This is also the region where the permittivity changes rapidly with the amount polypyrrole in the composite and so a high degree of control is required for reproducible making the same formulation. At the conductivities required for microwave absorption, the dc conductivity dominates and the ac component is negligible. Polypyrrole stability is an issue for fabricating a radar absorber, and stability can be improved through a barrier protecting the polypyrrole from oxygen.

Future work on radar absorbing materials will include the following materials:

1. The study of polypyrrole coated fabrics as the resistive layers in a Jaumann absorber, as a netting, or as part of structural RAM.

2. Combining polypyrrole powders with a binding matrix. These materials will be used for the production of Dallenbach layers, and as ink for printing resistive sheets to be used in the fabrication of Jaumann layers.

3. Composites of injection moulded polypyrrole and polyvinylchloride should be also be studied for use as Dallenbach absorbers over complex shapes.

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List of symbols/abbreviations/acronyms/initialisms

DND	Department of National Defence
AQSA	Anthraquinone-2-Sulfonic Acid
DBSA	Dodecylbenze Sulfonic Acid
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
PANI	Polyaniline
PMMA	Polymethylmethacrylate
PPy	Polypyrrole
PS	Polystyrene
PSS	Polystyrene Sulphonate
PTSA	Para-Toluene Sulfonic Acid
T_g	Glass Transition Temperature
RAM	Radar Absorbing Material

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14. ABSTRACT

(U) Radar absorbing materials require resistive or magnetic materials that will convert the electromagnetic energy into heat. The electrical properties of polypyrrole make it a suitable candidate for a radar absorbing material. There are several simple ways to make the polymer with controlled conductivity, and many strategies to process it into a robust material. Interesting materials include polypyrrole–paint, polypyrrole–polyvinylchloride injection moulded composites and polypyrrole coated fabrics and fibres. The highest imaginary component of the permittivity for a polypyrrole composite occurs at the percolation threshold. This is also the region where the permittivity changes rapidly with the amount polypyrrole in the composite and so a high degree of control is required for reproducible making the same formulation. At the conductivities required for microwave absorption, the dc conductivity dominates and the ac component is negligible. Polypyrrole stability is an issue for fabricating a radar absorber, and stability can be improved through a barrier protecting the polypyrrole from oxygen. In this paper many aspects of the formulation and characterisation of polypyrrole materials are considered with an emphasis on its suitability as a microwave absorber.

(U) Les matériaux absorbant les ondes radar doivent renfermer des substances magnétiques ou résistives, qui convertiront l'énergie électromagnétique en chaleur. Grâce à ses propriétés électriques, le polypyrrole est un bon candidat pour servir de matière absorbant les ondes radar. Il existe plusieurs manières pour synthétiser le polymère avec une conductivité déterminée et plusieurs stratégies pour le transformer en un matériau robuste. Parmi les matériaux présentant un tel intérêt, on retrouve des peintures au polypyrrole, des composites moulés par injection de type polypyrrole/poly(chlorure de vinyle) et des tissus et des fibres enduits de polypyrrole. La partie imaginaire la plus importante de la constante diélectrique d'un composite à base de polypyrrole est obtenue au seuil de percolation. C'est également la région où cette constante diélectrique varie rapidement en fonction de la quantité de polypyrrole dans le composite, et il est donc indispensable d'avoir un très bon contrôle du procédé pour obtenir une formulation reproductible. Aux conductivités requises pour l'absorption des micro–ondes, la conductivité c.c. prédomine, et la conductivité c.a. est négligeable. La stabilité du polypyrrole pose un problème lors de la fabrication d'un absorbant radar, et cette stabilité peut être améliorée au moyen d'une barrière protégeant le polypyrrole de l'oxygène. Dans le présent article, on rapporte divers aspects de la formulation et de la caractérisation des matériaux à base de polypyrrole, en mettant l'accent sur leur capacité à servir d'absorbant radar.

15. KEYWORDS, DESCRIPTORS or IDENTIFIERS

(U) Polypyrrole, Chemical synthesis, Electrochemical synthesis, Processability, solutions, Chemical composites, Copolymers, Graft Copolymers, Textiles, Microwave properties, Latex, Core Shell, Spectroscopy, IR, Raman, Permittivity, Conductivity, Stability, Radar Absorbing Material